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OXIDATION OF AROMATIC HYDROCARBONS

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The invention relates to the oxidation of aromatic hydrocarbons.

It is already known to oxidize to hydroperoxides alkyl-substituted or cyclohexyl-substituted benzenes having a structure:

$$C_6H_5—R$$

in which R is an alkyl group, having a CH group adjacent to the benzene ring, or in which R is a cyclohexyl group. It should be noted that the benzene ring may contain other substituents, such as additional alkyl groups. The oxidation has been carried out using a gas containing free oxygen. For example, it is known to oxidise cumene to cumene hydroperoxide.

When the oxidation is carried out in this manner, a substantial amount of undesirable by-products is obtained. For example, when cumene is used as the starting material, substantial amounts of acetophenone and alpha, alpha-dimethylbenzyl alcohol are formed in addition to the desired product, namely alpha, alpha-dimethylbenzyl hydroperoxide (i. e. cumene hydroperoxide).

It has been proposed to carry out the oxidation in the liquid phase under anhydrous conditions, by contacting the aromatic hydrocarbon with a gas containing free oxygen in the presence of a peroxide oxidation initiator capable of initiating a free radical oxidation chain. In the oxidation of cumene, a suitable oxidation initiator is, for example, cumene hydroperoxide.

In the oxidation of, for example, cumene to alpha, alpha-dimethylbenzyl hydroperoxide, it has already been disclosed that beneficial results are obtained by the presence of alkali metal and alkaline earth metal hydroxides, alkoxides, borates, phosphates and carbonates. It is believed that these alkaline compounds inhibit the development of acidity in the reaction, and hence, since hydroperoxides are decomposed by acids, stabilise the hydroperoxides against decomposition. Additives of the type disclosed above are referred to in this specification as "alkaline stabilising agents." It has also been proposed to use as alkaline stabilising agents alkali metal salts of weak organic acids, for example, those acids which form soaps, such as stearic acid, oleic acid, palmitic acid, lauric acid, linoleic acid and ricinoleic acid.

We have found that results markedly superior to those obtained in the processes of the prior art are obtained by employing two or more alkaline stabilising agents simultaneously, the alkaline stabilising agents being selected as hereinafter disclosed.

Thus, according to the present invention, there is provided a process for the production of tertiary hydroperoxides, which comprises the step of contacting an aromatic hydrocarbon, having a structure: Ar. R, where Ar is a phenyl group or a substituted derivative thereof, and R is either an alkyl group having a CH group adjacent to the aromatic nucleus, or a cyclohexyl group, in the liquid phase with a gas containing free oxygen, in the presence of a peroxide oxidation initiator capable of initiating a free radical oxidation chain, and an alkaline stabilising agent selected from the group consisting of carbonates of the alkali or alkaline earth metals or magnesium, and a second alkaline stabilising agent selected from weak organic acid salts of the alkali or alkaline earth metals or magnesium.

The peroxide oxidation initiator which is preferably an aralkyl hydroperoxide may be added to the aromatic hydrocarbon, or it may be produced in situ. For example, cumene, which has been stored in contact with air, contains a quantity of cumene hydroperoxide sufficient to initiate subsequent oxidation according to the process of the present invention. Alternatively, cumene hydroperoxide may be introduced into the cumene to be oxidised by recycling to the cumene a small quantity of cumene hydroperoxide from a previous run.

The alkaline stabilising agents may be added to the reaction mixture or they may be produced in situ. For example, sodium stearate may be produced in situ by adding sodium carbonate and stearic acid to the reaction mixture.

By using two alkaline stabilising agents simultaneously, we have found that a surprisingly higher rate of reaction is obtained than when using either of the stabilising agents alone. For example, in the oxidation of cumene using air as the oxidising gas at a rate of 25 to 30 litres per hour per litre of cumene, and operating at a temperature of 80° C., the following results were obtained:

Additive, based on weight of cumene	Yield of cumene hydroperoxide	Percent by weight of cumene reacted per hour
1% by wt. Na_2CO_3	90	0.23
0.5% by wt. sodium stearate	90	0.46
0.5% by wt. sodium stearate+1% by wt. Na_2CO_3	91	0.85

From these results, it is clear that by using a mixture of two alkaline stabilising agents, a considerably greater percentage of cumene is reacted in unit time than when either of the stabilising agents is used alone. The result of this marked improvement in the amount of cumene reacted gives rise to a greater output of cumene hydroperoxide per hour per unit volume of reaction space. Hence, economic advantages are obtained by operating according to the process of the present invention; to produce a given quantity of a hydroperoxide, a shorter time of operation or a decreased size of reaction vessel may be employed.

In operating according to the process of the present invention, the quantities of carbonate and salt of a weak organic acid may be varied over a wide range; in general, quantities of 0.1 to 2.0% by weight, based on the weight of aromatic hydrocarbon employed, are suitable. In particular, it is preferable to use of the order of 0.5% to 1.0% by weight of a salt of a weak organic acid and 1.0% by weight of carbonate.

Salts of weak organic acids, which may be used in the process of the present invention, are alkali metal, alkaline earth metal and magnesium derivatives of the weak organic acids which form soaps; preferably, the organic acid is free of olefinic unsaturation; suitable acids are stearic acid, palmitic acid, lauric acid, or the mixture of saturated fatty acids obtained by the hydrolysis of fats.

Aromatic hydrocarbons which may be used in the process of the present invention include, for example, cumene, cymenes, di-isopropyl benzenes, sec.-butyl benzenes and cyclohexylbenzene.

The peroxidic oxidation initiator employed is conveniently the peroxide corresponding to the aromatic hydrocarbon to be oxidized; for example, when cumene

is the starting material, a convenient initiator is cumene hydroperoxide.

The process of the present invention may be carried out by passing air or oxygen through the aromatic hydrocarbon containing the oxidation initiator and alkaline stabilising agents. The reaction is carried out at an elevated temperature; for example, cumene is preferably reacted at a temperature of 50° to 100° C. The optimum temperature of operation is 79° to 80° C.; below this temperature the reaction rate is low, while at temperatures in excess of 80° C., the formation of deleterious by-products is increased to an undesirable extent.

In order to obtain the optimum yield of hydroperoxide, it is desirable to restrict the reaction time so that the hydrocarbon is not completely converted. For example, when using a mono-alkyl benzene, such as cumene, as the starting material it is advantageous to stop the reaction after at most 40% to 50% of the hydrocarbon has been oxidized.

As a feature of the present invention, the reaction may be carried out in the presence of suitable inert diluents; diluents which may be used include monochlorobenzene, mixtures of di-chlorobenzenes, higher chlorinated benzenes of the type which may be produced as by-products in the chlorination of benzene to chlorobenzene, and tetra-chloroethane. The use of diluents is particularly advantageous when oxidising hydrocarbons which contain two groupings capable of being oxidised to hydroperoxide groupings. Thus it is particularly desirable to use a diluent in the oxidation of para di-isopropyl benzene to para di-isopropyl benzene di-hydroperoxide. In carrying out reactions of this type, it is desirable to operate at the highest conversion of the starting material which is possible, without producing deleterious quantities of by-products, and the presence of a diluent enables operation at a higher conversion than in the absence of a diluent for the same amount of by-product formation. When using a diluent it is possible to operate at a higher temperature than when operating in the absence of a diluent; for example, when oxidising para di-isopropyl benzene to para di-isopropyl benzene di-hydroperoxide, the optimum reaction temperature is about 80° C. in the absence of the diluent and about 90° to 100° C. when a diluent is used.

When it is desired to produce a di-alkyl benzene di-hydroperoxide, it is convenient to separate the di-alkyl benzene di-hydroperoxide from the reaction product and to recycle the remaining mixture of unchanged hydrocarbon, mono-hydroperoxide, solvent, if one is employed, additional di-alkyl benzene and possibly additional stabilising agents to the reaction zone. In this way, the initial hydroperoxide content of the reaction mixture is conveniently provided. Furthermore, it is undesirable in this reaction to operate at a high conversion to di-hydroperoxide, since in this case the yield of di-hydroperoxide diminishes. By carrying out the reaction in a recycle process as stated, it is possible to avoid high conversion to di-hydroperoxide and, in consequence, to avoid low yields of di-hydroperoxide.

The peroxides produced by the process of the present invention may be used, for example, as accelerators for polymerisation or oxidation reactions. They are also important intermediates in the production of phenols and ketones. For example, cumene hydroperoxide may be converted by treatment with a mineral acid or with an activated earth, or on alumina-silica gel, to phenol and acetone.

EXAMPLE 1

The reactor employed was a glass tower, 2.2 inches in diameter and 12 inches long, with a gas inlet in the centre of the bottom. The gas entered the reaction zone through a piece of fritted glass, which was fitted into the bottom of the reactor. This ensured good gas distribution. The reactor was connected to a reflux condenser, and was heated in a thermostatically controlled water bath. A stirrer was employed to keep the additives well dispersed in the reaction mixture.

The reactor was charged with 200 mls. of cumene, containing 1% by weight of cumene hydroperoxide and the desired amounts of sodium carbonate and sodium stearate. In order to increase its surface area, and to facilitate its dispersion in the liquid, the sodium carbonate was ground in a ball mill prior to use, and sieved through a 200 B. S. S. sieve (aperture size, 0.076 mm.).

The reaction mixture was heated to a temperature of 80° C., and air was passed through at a rate of 5 to 6 litres per hour.

The results given in the Table I below were obtained. Comparative figures are given for the reaction in the presence of no additive, sodium carbonate and sodium stearate alone.

Table I

Additive (percent by wt.)	Reaction time (Hours)	Amount of hydroperoxide formed (Percent by wt. of product)	Rate of formation of hydroperoxide (percent wt. per hour)	Yield of hydroperoxide based on cumene attacked (percent)
Nil	49	18.6	0.38	89
1% Na_2CO_3	73	16.7	0.23	90
0.5% Sodium stearate	93	43	0.46	90
0.2% Sodium stearate+1.0% NA_2CO_3	76	40.2	0.53	91
0.5% Sodium stearate+0.5% Na_2CO_3	70	44.0	0.63	90
1.0% Sodium stearate+0.5% Na_2CO_3	50	43.0	0.86	90
1% Sodium stearate+1% Na_2CO_3	46	40.0	0.87	91
0.5% Sodium stearate+1% Na_2CO_3	48	41.0	0.85	91

EXAMPLE 2

Reactions were carried out as in Example 1, using charges of 200 ml. of cumene with an initial cumene hydroperoxide content of 1% by weight. The time of reaction was in each case 48 hours, the temperature of operation 80° C. and air was passed through the reaction mixture at a rate of 6 litres per hours. The results obtained, including details of the additives employed, are given in Table II below.

Table II

Additive (percent by wt.)	Peroxide content (percent by wt. of product)	Rate of peroxide formation (percent wt. per hour)	Yield as peroxide content of oxidised material (percent by wt.)
Nil	18.6	0.37	89
1% Na_2CO_3	16.5	0.32	97
0.5% Na stearate	29	0.58	90.5
1% Na_2CO_3 +0.5% Na stearate	41	0.83	91

The results clearly show the beneficial influence of having both sodium stearate and sodium carbonate present at the same time.

EXAMPLE 3

Example 2 was repeated using an additive comprising 0.5 grams of calcium stearate and 1 gram of calcium carbonate per 100 ml. of cumene. At the end of 48 hours the reaction product conatined 36.8% by weight of cumene hydroperoxide. The yield of peroxide expressed as the percent by weight of peroxide, based upon the total amount of oxidised products obtained, was 91%. It will be seen that the results, using calcium stearate in conjunction with calcium carbonate as additives, are similar to those obtained when using comparable quantities of sodium stearate and sodium carbonate (see Example 2).

EXAMPLE 4

Samples of 100 ml. of di-isopropyl benzene (95% of the para isomer), 100 ml. of mono-chlorobenzene and 2 grams of para di-isopropyl benzene di-hydroperoxide were heated to 90° C. and oxygen was passed through at a rate of 15 litres per hour. The duration of the reaction was 7.3 hours. Each of the samples employed contained an additive as shown in Table III.

Table III

Additive (percent by wt.)	Final product content (as percent wt./vol. mono-peroxide)	Average reaction rate (percent wt./vol. of mono-peroxide per hr.)	Yield as peroxide content of oxidised mixture (percent by wt.)
2% Na_2CO_3	9	1.2	
2% sodium stearate	27.3	3.7	63.0
1% Na_2CO_3+1% sodium stearate	38.6	5.3	76.5

It will be seen that when using an additive comprising sodium stearate together with sodium carbonate a considerably higher reaction rate was obtained than when using sodium stearate or sodium carbonate alone.

EXAMPLE 5

In this example the para di-isopropyl benzene employed contained 95% of the para isomer.

A mixture of 34.4 grams of di-isopropyl benzene, 176 grams of chlorobenzene, 2 grams of para-di-isopropyl benzene di-hydroperoxide, 2 grams of sodium carbonate and 2 grams of sodium stearate was heated to 100° C. and oxygen was passed through this mixture at a rate of 10 litres per hour for 26 hours.

From the product 20.5 grams of a solid precipitate were obtained. This precipitate contained 69% of para di-isopropyl benzene di-hydroperoxide. The liquid portion of the product weighed 160 grams and contained 12% by weight of di-isopropyl benzene mono-hydroperoxide.

To 137 grams of the liquid product, 9.5 grams of di-isopropyl benzene, 1.4 grams of sodium carbonate and 1.4 grams of sodium stearate were added. This mixture was heated to 100° C. and oxygen was passed through at a rate of 10 litres per hour for 25 hours. 14.7 grams of a solid product were obtained which contained 70% by weight of di-isopropyl benzene di-hydroperoxide. The liquid portion of the product weighed 109 grams and contained 12% by weight of para di-isopropyl benzene mono-hydroperoxide.

In the second stage of this reaction it will be seen that the initial and final mono-peroxide contents were approximately the same, the loss in volume of the reaction mixture being due to mechanical losses on the small quantities of reactants employed. Therefore the process was essentially one in which 9.0 grams of para di-isopropyl benzene were converted to 10.3 grams of para di-isopropyl benzene di-hydroperoxide. This corresponds to a yield of 81% of theory.

What is claimed is:

1. A process for the production of tertiary hydroperoxides from aromatic hydrocarbons having the structure:

Ar—R

wherein Ar is an aromatic radical selected from the group consisting of phenyl and substituted phenyl and R is an aliphatic hydrocarbon radical selected from the group consisting of secondary alkyl and cyclohexyl and in which said aliphatic hydrocarbon radical is chemically bonded to said aromatic radical through a secondary carbon atom, which comprises the step of contacting said aromatic hydrocarbon in the liquid phase under anhydrous conditions with a gas containing free oxygen and in

the presence of a peroxide oxidation initiator capable of initiating a free radical oxidation chain reaction and a first alkaline stabilizing agent consisting essentially of a carbonate of a metal selected from the group consisting of alkali metals, alkaline earth metals and magnesium, and a second alkaline stabilizer agent consisting essentially of a metal salt of a soap-forming weak organic acid, said metal being selected from the group consisting of alkali metals, alkaline earth metals and magnesium, said first alkaline stabilizing agent and said second alkaline stabilizing agent each being present in the reaction mixture in an amount from about 0.1% to about 2% of the weight of said aromatic hydrocarbon.

2. The process of claim 1 wherein said carbonate salt is present in an amount of about 1% of said aromatic hydrocarbon.

3. The process of claim 1 wherein said soap-forming weak organic acid is free from olefinic unsaturation.

4. The process of claim 1 wherein said first alkaline stabilizing agent and said second alkaline stabilizing agent are present in the ratio of from 1:2 to 2:1.

5. A process as claimed in claim 1 in which the reaction is carried out in the presence of an inert diluent which is a chlorinated hydrocarbon selected from the group consisting of mono-chlorobenzene, di-chlorobenzenes, higher chlorinated benzenes and tetra-chloroethane.

6. A process as claimed in claim 1 in which said soap-forming weak organic acid is selected from the group consisting of stearic acid, palmitic acid, lauric acid and the mixtures of saturated fatty acids obtained by the hydrolysis of fats.

7. A process as claimed in claim 1 in which said metal is sodium.

8. A process as claimed in claim 1 in which the peroxide oxidation initiator is an aralkyl hydroperoxide.

9. A process for the production of tertiary hydroperoxides which comprises the step of contacting an aromatic hydrocarbon selected from the group consisting of cumene, cymenes, di-isopropyl benzenes, sec. butyl benzenes and cyclohexyl benzene, in the liquid phase under anhydrous conditions with a gas containing free oxygen, in the presence of a peroxide oxidation initiator capable of initiating a free radical oxidation chain and an alkaline stabilising agent consisting of a carbonate of a metal selected from the group consisting of alkali metals, alkaline earth metals and magnesium, and a second alkaline stabilising agent, which is a weak soap-forming organic acid salt of a metal selected from the group consisting of alkali metals, alkaline earth metals and magnesium, said stabilizing agents each being present in an amount from about 0.1% to about 2% of the weight of said aromatic hydrocarbons.

10. A process as claimed in claim 9 in which the aralkyl hydroperoxide to be used as peroxide oxidation initiator is supplied by recycling a minor amount of aralkyl hydroperoxide from the previous oxidation step.

11. A process as claimed in claim 9 in which the reaction is carried out at a temperature within the range of 50° to 100° C.

12. A process as claimed in claim 9 in which the reaction is carried out at a temperature of 79° to 80° C.

13. A process as claimed in claim 9 in which the reaction is carried out for a length of time such that the hydrocarbon is incompletely converted to oxidation products.

14. A process as claimed in claim 9 in which the dialkyl benzene is converted to a dialkyl benzene di-hydroperoxide by reacting the dialkyl benzene in the presence of a solvent with oxygen, characterized in that the reaction is carried out in a manner such that a substantial proportion of the hydrocarbon remains unconverted dialkyl benzene di-hydroperoxide is separated from the reaction product, and dialkyl benzene monohydroperoxide together with unchanged dialkyl benzene, and, fresh quantities of

alkaline stabilizing agents, are returned together with additional dialkyl benzene to the reaction zone.

15. A process for the production of tertiary hydroperoxides which comprises the step of contacting an aromatic hydrocarbon having the structure:

Ar—R

wherein Ar is an aromatic radical selected from the group consisting of phenyl and substituted phenyl and R is an aliphatic hydrocarbon radical selected from the group consisting of secondary alkyl and cyclohexyl and in which said aliphatic hydrocarbon radical is bonded to said aromatic radical through a secondary carbon atom, in the liquid phase under anhydrous conditions with a gas containing free oxygen and in the presence of a peroxide oxidation initiator capable of initiating a free radical oxidation chain reaction and a first alkaline stabilizing agent consisting essentially of a carbonate of a metal selected from the group consisting of alkali metals, alkaline earth metals and magnesium, and a second alkaline stabilizer agent consisting essentially of metal salts of soap-forming weak organic acids, said metal being selected from the group consisting of alkali metals, alkaline earth metals and magnesium, wherein said first alkaline stabilizing agent is present in the reaction mixture in an amount from about 0.1% to about 2% of the weight of the said aromatic hydrocarbon and wherein said second alkaline stabilizing agent is present in an amount from about 0.5% to about 1% by weight of said aromatic hydrocarbon.

16. A process for treating an anhydrous liquid mixture containing a secondary alkyl substituted monocyclic aromatic hydrocarbon, a peroxide free radical oxidation chain initiator, a metal carbonate salt, present in an amount from about 0.1% to about 2% by weight of said aromatic hydrocarbon and a metal salt of a weak soap-forming organic acid present in an amount from about 0.1% to about 2% by weight of said aromatic hydrocarbon, said metal being selected from the group consisting of alkali metals, alkaline earth metals, and magnesium, said process comprising passing a gas containing free oxygen through said liquid mixture whereby tertiary hydroperoxides are produced.

17. A process for the oxidation of an aromatic hydrocarbon, having the formula:

Ar—R

wherein Ar is an aromatic radical selected from the group consisting of phenyl and substituted phenyl and R is a secondary aliphatic hydrocarbon radical selected from the group consisting of alkyl and cyclohexyl, and being bonded to said aromatic radical through a secondary carbon atom, to a tertiary hydroperoxide, said process comprising passing a gas containing free oxygen through a liquid phase under anhydrous conditions, said liquid phase comprising said aromatic hydrocarbon, a peroxide oxidation initiator capable of initiating a free radical oxidation chain, an alkaline stabilizing agent consisting essentially of a metal carbonate present in an amount from about 0.1% to about 2% of the weight of said aromatic hydrocarbon, and an alkaline stabilizing agent consisting essentially of a metal salt of a soap-forming organic acid present in an amount from about 0.5% to about 1% of the weight of said aromatic hydrocarbon, said metal in each instance being selected from the group consisting of alkali metals, alkaline earth metals, and magnesium.

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